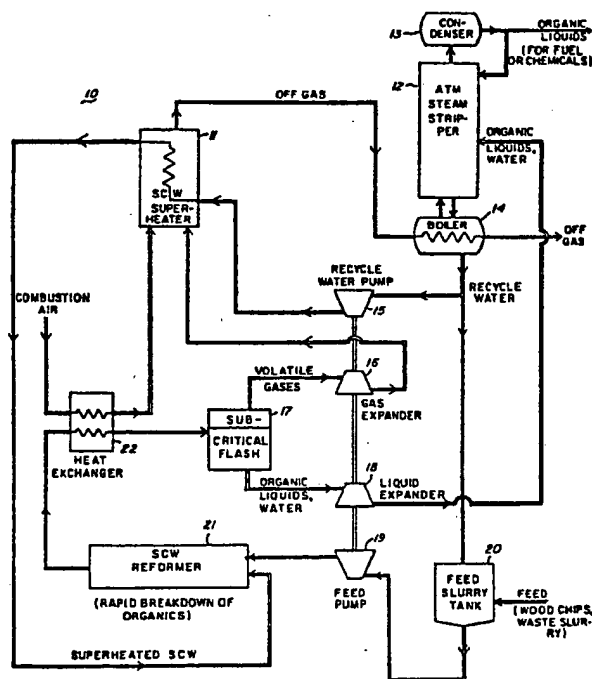




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(54) Title: TREATMENT OF ORGANIC MATERIAL IN SUPERCRITICAL WATER



## (57) Abstract

Organic materials are treated in water in the region of the critical density of water, to restructure the feed organic materials to form resulting organic materials including non-toxic materials from toxic starting materials, and useful volatile organic liquids. Solid materials and viscous liquid materials are restructured to form liquid fuels or other useful liquid products. Toxic materials are restructured to make them non-toxic in various processing schemes.

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1        TREATMENT OF ORGANIC MATERIAL IN SUPERCRITICAL WATER

Background of the Invention

          A number of alternate routes have been and are still being de-  
veloped for converting organic feed materials such as coal and cellu-  
5        losic materials including forest products, to liquid and gaseous  
fuels. Among the approaches are pyrolysis, gasification with steam  
and oxygen to form synthesis gas and liquefaction with hydrogen,  
carbon monoxide or hydrogen donor solvents. Each of these approaches  
have one or more drawbacks. In pyrolysis, there is a problem with  
10       the feed ending up as char in certain instances. In steam-oxygen  
gasification, high temperatures are necessary as for example 800 to  
1000°C and the process thus requires considerable high-temperature  
heat. Liquefaction with hydrogen or carbon dioxide requires a  
separate processing step to supply these materials in relatively large  
15       quantities.

          The prior art has also converted organic liquids to fuels by  
reaction with water, as for example, by reforming petroleum fractions  
catalytically to methane and carbon dioxide by a reaction with steam  
at 20 to 40 atmospheres. This avoids the use of a high temperature  
20       heat source and has met with some success where it is desirable to  
convert organic liquids to gaseous products.

          In a still more recent development, it has been suggested that  
liquid or solid organic materials can be converted to high BTU gas  
with little or no formation of undesirable char or coke when the  
25       organic material is reacted with water at a temperature at or above  
the critical temperature of water and at or above the critical pressure  
of water to achieve the critical density of water as for example set  
forth in United States Patent 4,113,446.

          In that patent, feed material was indicated to be converted to  
30       gaseous products in an amount of about 8 to 10% after one hour in a



1 batch autoclave. In this prior gasification process, when a variety  
of reforming catalysts were used, 20 to 25% of the feed carbon could  
be gasified in relatively short times as for example 30 minutes. The  
formation of char can easily be avoided and useful high BTU gas is  
5 produced. However, as indicated in that patent, organic feeds were  
not completely transformed to gaseous products having high fuel  
value even after substantial periods of time at supercritical condi-  
tions. Attempts to separate substantial organic liquid products with  
methylene chloride resulted in recovery of only a small fraction,  
10 often no more than 6%, of liquid products, see Reforming of Glucose  
and Wood at The Critical Conditions of Wood, a paper presented at  
Intersociety Conference on Environmental Systems July 11-14, 1977,  
San Francisco, California, published by ASME, 1977. These results  
indicated that organic products could not be separated on a commercial  
15 scale.

#### Summary of the Invention

It has now been found that when organic materials are dispersed  
in water and brought to supercritical conditions, the organic materials  
are rapidly broken down and restructured to form organic materials  
20 which have structures and properties which are different from those  
of the feed materials. Only some of the restructured products  
appear as gases such as CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub> while the major portion  
of the products resulting are relatively volatile liquids. The gaseous  
as well as the volatile organic liquid products can be relatively easily  
25 separated from the water by reducing temperature and pressure below the  
critical conditions of the reaction mixture and then carrying out con-  
ventional separation steps.

It is an object of this invention to use the reaction of organic  
materials with water in the region of the critical density of water to  
30 reform the organic materials and obtain useful volatile organic liquid  
materials.

It is a still further object of this invention to provide a method  
of reacting toxic organic materials with water in the region of the  
critical density of water to obtain non-toxic organic materials which  
35 reaction can be carried out when the toxic materials are in sub-



1   stantially pure form or appear as trace or other amounts in other  
materials such as river water, lake water or other mixtures to be  
purified.

5       According to the invention, an organic material which can be  
solid or liquid is treated by reacting in water to restructure the  
organic material and form resulting organic material. The feed  
organic material is admixed with water to form a reaction mixture  
for a time period while maintaining the water in the region of its  
critical density preferably by the use of a temperature at least as  
10   high as about the critical temperature of water and a pressure  
at least as high as about the critical pressure of water to form  
resulting more volatile organic material than the feed organic  
material which resulting material is selected from the group consist-  
ing essentially of non-toxic organic materials where the original  
15   feed material was toxic, and useful volatile organic liquids. The  
useful volatile organic liquids are recovered in amounts of at least  
25 weight percent of the feed organic material.

20       Preferably, the organic material is a toxic material or a  
toxic material in at least trace amounts in a mixture as for example  
river water and the resulting product is a non-toxic material as  
for example cleansed water containing lower molecular weight organic  
materials which are non-toxic.

25       In another preferred process in accordance with this invention,  
the original organic material is a solid or heavy liquid material  
and the resulting products are lower molecular weight volatile  
organic liquids which can be used as fuels or for other purposes.

30       Preferably, the process is carried out by bringing the react-  
ing temperature to at least 374°C rapidly and preferably substan-  
tially instantaneously to avoid the formation of char. When toxic  
materials are treated by the process of this invention, the resulting  
products may be safely discarded if no commercially useful products  
are formed.

35       The separation techniques for separating useful products from  
the reaction mixture include distillation, flashing, decanting and  
membrane separation.

It is a feature of this invention that the liquid products formed



1 can be hydrophobic and can have volatilities such that they will distill off before water and thus be easily separated in distillation procedures. The term "volatile" as used in this application with reference to organic liquids means organic products which have a vapor pressure no less than 1/10 that of water at any temperature in the range of 25°C to 374°C.

Description of Preferred Embodiments

In accordance with the invention, organic material is restructured in water to form different organic materials which include volatile organic liquids and in some cases, non-toxic, organic materials which may or may not be volatile liquids.

The process can be carried out in batch or continuous operations. For example, the process can be carried out in an autoclave as described in U.S. Patent 4,113,446. Continuous methods can be used where a reaction slurry or liquid mixture of the reactants and water is treated under heat and pressure. A feed mixture of organic material to be treated is preferably brought to temperature of reaction as stream to a flow of superheated water, heated for example to 600 to 900°C, to quickly and substantially instantaneously bring the organic material feed to temperature. The quick heating of the feed minimizes or substantially eliminates char formation.

The reaction conditions are such that the organic material feed is used in an amount up to about 25 weight percent of water and preferably from about 5 to 10 weight percent of water. Low concentrations may be used, as for example fractional percentages, in reforming toxic materials to non-toxic material as for example in the detoxification and purification of contaminated surface water or well water. Catalysts can be used during the reaction to promote reforming and hydrogenation of organic materials as well as to facilitate simple breakdown of organic chains. Representative suitable catalysts include nickel, molybdenum, cobalt, their oxides or sulfides, and noble metal catalysts such as platinum, palladium or the like or mixtures thereof either unsupported or supported on a base such as silica, alumina mixtures thereof and the like.

1 The reaction often preferably is carried out at the critical  
density of water which means that the temperature must be at least  
the critical temperature and the pressure at least the critical pres-  
sure of water. Parameters at the near critical condition of water  
5 can also be used and should be considered the equivalent of exact  
critical condition. Thus, as referred to herein, the terms "sub-  
stantially at its critical density", "about its critical temperature"  
and "about its critical pressure" refer to water in the near critical  
region. The near critical region or the term "in the region of  
10 the critical density of water" is encompassed by densities of from  
0.2 to 0.7 grams per centimeter<sup>3</sup>. In this near critical region or  
in the region of the critical density, pressures can be from 200 to  
2500 atmospheres and temperatures can be from 374°C to at least 450°C.  
A critical temperature range of 374°C to 450°C and a critical density  
15 range of .3 to .55 grams per centimeter<sup>3</sup> are preferred for use.

While the reactions can be carried out in batch operations over  
long time periods of several hours, most efficient operation is achieved  
by rapid reaction over time periods of no more than 15 minutes and  
preferably from 1 to 10 minutes in flow-through, continuous reactors.

20 Toxic material which can be treated by reaction with water under  
critical conditions include those on the EPA toxic chemical list of  
toxic organic substances as for example:

Aldrin  
Dieldrin  
25 DDT  
2,4,5-T and esters  
2,4-diaminotoluene  
Lindane  
p-Aminobenzoic acid  
30 Anthranilic acid



1                    Alfatoxin  
                     Heptachlor  
                     Malathion  
                     Nitrosamines

5            When toxic chemicals are treated under critical conditions in  
the process of this invention, restructuring of the toxic chemical  
occurs to form non-toxic materials. As used in this application,  
toxic materials are those recognized as hazardous by the U.S. Environ-  
mental Protection Agency as for example those set out in EPA publi-  
10 cation EPA-560/11-79-001 entitled Test Data Development Standards:  
Chronic Health Effects Toxic Substances Control Act; Section 4.  
The reaction mixture after reaction can then be discarded safely.  
In some cases, the resulting materials can be removed as by biological  
oxidation, activated carbon adsorption and the like before discarding  
15 or reusing the remaining water. In other cases, the non-toxic prod-  
ucts which result from reformation of the toxic organic starting  
materials can be used for commercial purposes. For example, volatile  
liquids formed can be used as fuels. It is found that since toxicity  
is highly structure-specific, simple altering of one or more chemical  
20 bonds in many organic toxic materials results in products which are  
non-toxic and which can be safely disposed of.

          The non-toxic starting materials which are to be reformed by the  
process of this invention for use as fuels or for other commercial pur-  
poses, can be a wide variety of starting materials. Solid organics  
25 include coal or organic waste materials, cellulose, waxes, coal tars,  
shale, wood products including trees, leaves, bark and the like.  
Liquid organic materials including aryl or acyl hydrocarbons such as  
petroleum fractions up to and including asphalt fractions, aromatic  
hydrocarbons, sugars, black liquor from pulping of wood, green liquor  
30 used to pulp, organic acids, alcohols, aldehydes, ketones, amines,





1 mixtures thereof and the like can be used.

5 The reaction is preferably effected by continuously intimately contacting the organic feed material with water. When employing solid organic material such as coal or organic waste material, it is preferred that the solid be in the form of small particles and the reaction be conducted so that the organic particles in water are fed to the reactor as a slurry. In order to promote intimate contact, the solid particles can be small and in the order of from submicron size to about 1 cm. Larger particles can be employed in some cases.

10 In a specific example of this invention, a flow reactor was used with a one weight percent solution of glucose in water. At a flow rate of about 10 ml per minute, the feed solution was heated rapidly to supercritical conditions by pumping to 315 atmospheres and then passing the mixture through a feed preheater, which was constructed of 10 feet of 3/32 inch, inside diameter, stainless steel tubing im-  
15 mersed in a molten lead bath at 380°C. A residence time of less than 20 seconds was required to reach 374°C; within one minute, the feed was brought to essentially the temperature of the lead bath. Following preheat, the mixture was maintained at the supercritical  
20 conditions of 315 atmospheres and 380°C for a residence time of about 7 to 11 minutes in a reactor consisting of a ten foot section of 5/16 inch, inside diameter, stainless steel tubing, which was also maintained at constant temperature by immersion in the molten lead bath. The products were then passed through a water-cooled heat exchanger to  
25 bring the resulting mixture to room temperature and then to a throttling valve to bring the mixture to atmospheric pressure. Liquid and vapor phases were separated and the flow rates of each of these phases was measured. Samples of the vapor phase were analyzed by gas chromatography and the liquid phase was analyzed for total carbon. The  
30 results are shown in Tables 1 and 2.



TABLE 1  
UNCATALYZED GAS RESULTS

DENSITY (g/cm <sup>3</sup> )	RESIDENCE TIME(min)	GAS PRODUCTION (ml/ml feed)	GAS PHASE CARBON (%) of feed)	GAS COMPOSITION(percent by volume) <sup>b</sup>						RUN NO.
				H <sub>2</sub>	N <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	
0.375	8.29	0.768	7.71	16.1	2.0	40.4	0.91	37.1	0.97	1
0.55	7.47	0.883	9.29	14.5	1.3	37.1	0.77	41.5	2.44	2
0.55	9.59	0.916	9.66	13.7	1.8	39.7	0.73	39.9	2.03	3
0.55	10.26	0.947	9.99							4
0.55	9.63	0.946	9.92	14.3	1.5	37.7	0.75	41.3	2.1	5
0.55	10.69	1.020	10.51	15.0	2.0	35.4	0.69	42.4	2.0	6
0.60	9.50	0.999	10.41	15.0	1.5	34.9	0.65	43.1	2.39	7
<sup>a</sup> 0.32	8.44	1.515	14.9	19.6	0.7	33.7	0.72	42.2	0.89	8
<sup>a</sup> 0.32	8.09	1.507	14.8							9
<sup>a</sup> 0.50	7.63	1.575	16.4	15.0	1.2	38.4	0.70	40.3	1.91	10
<sup>a</sup> 0.50	7.19	1.555	16.2							11

a) These runs are at 410°C. All others are at 380°C.

b) Water content of gas = 2.5%.



TABLE 2  
UNCATALYZED LIQUID RESULTS

RUN NO.	DENSITY (g/cm <sup>3</sup> )	RESIDENCE TIME (min)	CH <sub>2</sub> Cl <sub>2</sub> EXTRACTIONS		LIQUID PRODUCT RESIDUE (wt % of feed)	LIQUID PRODUCTS EVAPORATED (wt % of feed)
			ACIDIC (weight % of feed)	BASIC (weight % of feed)		
1	0.375	8.29	5.6	4.6	25.6	66.7
2	0.55	7.47	9.3	0.8	24.5	66.2
3	0.55	9.59	6.6	0.6	25.1	65.2
5	0.55	9.63	6.6	1.5	20.1	70.0
6	0.55	10.69			26.4	63.1
7	0.60	9.50	6.2	0.8	22.1	67.5
9 <sup>a</sup>	0.32	8.09	9.5	3.5	11.6	73.6
10 <sup>a</sup>	0.50	7.63	5.7	1.5	12.6	71.0

a) These runs are at 410°C. All others are at 380°C.



1        At 380°C with these short residence times as indicated in  
the Tables, 7 to 10% of the feed organic material was gasified  
(Table 1, runs 1-7). This gasification is as much as had previously  
5        been observed for a one-hour residence time in batch autoclave experi-  
ments with glucose. The observation that a significant quantity of gas  
can be obtained at a short residence time under supercritical conditions  
is the indication of the occurrence of rapid breakdown and restruc-  
turing of the feed organic material.

      Attempts were made to extract the organic liquid products so  
10       that they could be analyzed by a combination of gas chromatography,  
liquid chromatography and mass spectrometry. In prior work, a  
variety of solvents had been explored as extracting agents. Polar  
solvents could not be used because they are water-soluble. Methylene  
chloride was chosen because it is essentially immiscible with water  
15       and volatile enough so that the extracted products could be concentrated  
by evaporation of the solvent. In these prior tests, a 10 ml ali-  
quot of aqueous product was extracted with 5 ml of methylene chloride.  
After concentrating the extract to 0.1 ml, analysis of the concen-  
trate could account for no more than 0.5 to 6 weight percent of the  
20       carbon in the feed.

      In an attempt to improve the extraction efficiency of liquid  
products, separate 20 ml aliquots of the aqueous product were acidi-  
fied with 7 ml of 0.9 molar sulfuric acid and made basic with 7 ml of  
0.9 molar potassium hydroxide prior to extraction. Each aliquot was  
25       extracted with three 10 ml portions of methylene chloride. The ex-  
tracts were then air-dried at ambient temperature and the residue  
weighed. The results, shown in columns 4 and 5 of Table 2, were con-  
verted to percent by weight of feed material. The acidic extractions  
resulted in a somewhat higher recovery of liquid products than the  
30       basic extractions, but in both cases, the recovery efficiency was



1 extremely low (less than 10%).

To verify that the aqueous product actually contained significantly more organic liquid products than that which was extracted by methylene chloride, carbon analysis of feed and all products were  
5 made for run 3. Total carbon analyses were made for feed and liquid product and carbon content of the gaseous were calculated from the composition of the vapor, as determined by gas chromatography. The carbon content of the feed was found to be 0.42 weight percent, whereas the liquid product contained 0.36 weight percent and the vapor  
10 product 0.039 weight percent, for a total of 0.40 weight percent carbon in the products. Thus, it was established that the liquid products contained about 90% of the weight of the feed material, no more than 10% of which could be recovered by methylene chloride extraction.

15 The reaction mixture after 7 to 11 minutes of reacting, was evaporated at ambient temperature. The fraction of organics remaining after evaporation are shown in Table 2 column 6. Only 10 to 26% of the original carbon feed is accounted for in the residue. A large fraction of organic liquid products are volatile; at least as  
20 volatile as water, if not more so. Thus, the last column in Table 2 is the fraction of the carbon feed that was lost during evaporation of the water, i.e., from 63 to 74% of the carbon feed can be recovered as volatile organic liquids. These materials are readily separable from the aqueous product by distillation or sequential flashing or  
25 in some cases by other conventional separation techniques at sub-critical conditions. Moreover, these products are reformed products of the original organic feed and can be useful as fuels in their liquid or gaseous forms.

30 FIG. 1 illustrates a preferred flow diagram for a continuous process of reforming solid organic material to form liquid fuels and



1 chemicals as shown in FIG. 1 at 10. The supercritical water reformer  
is noted at 21 and is preferably sized as a tubular reactor with a flow  
therethrough such that the material to be reformed spends only from  
seconds to minutes under supercritical conditions to rapidly dissolve  
5 and disperse the solid matter in the feed and rapidly break down high  
molecular weight components into gases and volatile liquids such as  
hydrogen, carbon monoxide, methane, carbon dioxide and other reformed  
lower molecular weight volatile liquid organic compounds. Portions  
of the products produced may be oxidized within the overall processing  
10 scheme and utilized for internal energy requirements as in heating water  
to supercritical conditions.

FIG. 1 shows a wood chip process where a feed of wood chips is  
fed to a slurry tank 20 and suspended in water. Feed pump 19 pumps  
the feed to a supercritical water reformer 21 which also receives super-  
15 heated, supercritical water at high temperature so that the cold feed  
is instantly heated to supercritical conditions as previously described.  
A heat exchanger 22 is positioned in the line from the reformer 21  
so as to heat combustion air going to the furnace 11 which in turn heats  
the water to supercritical conditions for use in the reformer 21.  
20 The flow from the reformer 21, is brought to a subcritical flashing  
unit 17 which removes gaseous products to a gas expander 16 and in  
turn uses these gases in the heating process of the furnace 11. The  
flashing unit 17 is maintained somewhat below the critical tempera-  
ture of the aqueous solution, although the pressure may be above the  
25 critical pressure of water. Typically, the temperature may be 300 to  
350°C in flashing unit 17. Organic liquids and water are taken through  
a liquid expander 18 where liquids are passed to a steam stripper 12  
and condenser 13 arrangement which takes off organic liquids for use  
as fuel or chemicals. Off gases from the superheater 11 are passed  
30 to a boiler 14 which acts to aid in the stripping occurring in the  
stripper 12 while recycled water passes to water pump 15 for passage



1 to the water heater with some water passing to the feed slurry tank.

The feed can be mixed to the proper proportion in the feed slurry tank bearing in mind the additional superheated water that will be added in the reformer. No predrying of the feed is necessary. The slurry can be pressurized and heated to supercritical conditions very rapidly to avoid char formation. Heating can be obtained by mixing the feed with the superheated, supercritical water at 600 to 900°C or by heating along the line leading from the slurry tank to the reformer.

In all cases, short residence times of up to 15 minutes are preferably maintained in the supercritical water reactor.

FIG. 2 illustrates the processing of a slurry such as black liquor from pulping which contains relatively high concentrations of inorganic materials as well as organic materials. Black liquor from the holding tank 31 is pumped through pump 32 to the supercritical water reformer 33 which is maintained at near critical conditions and causes rapid breakdown of organics. The reformer 33 passes the reaction products to the heat exchanger 35 where heat is taken off to heat water passing to the supercritical water superheater 41 which water is in turn used in the reformer. Combustion air is used to heat the water in the superheater 41 along with combustible gases and volatile organics obtained from a flash drum number 2 at 40 with the oil phase from the flash drum passing to fuel storage. The feed from the reformer 33 after passing through heat exchanger 35 is reduced in pressure by a letdown valve 36 and then passed to flash drum number 1 at 38 whereupon an inorganic solution is removed through valve 42. Flash drum number 1 at 38 is maintained at temperatures and pressures below the critical conditions of water, where volatile organic material, gaseous products, and steam can be collected overhead. These conditions are typically in the range of 250 to 350°C and 30 to 150 atmospheres. The inorganic solution can be used to recover sodium and sulfur so as



1 to obtain an acceptable green liquor which is subsequently to be  
mixed with wood feed. The temperature and pressure of the overhead  
steam from flash drum number 1 are reduced further and fed to flash  
drum number 2 at 40 through a heat exchanger 37. The conditions  
5 in flash drum number 2 at 40 are typically ambient temperature to  
200°C and ambient pressure to 15 atmospheres. The aqueous phase con-  
taining hydrophilic organics is taken from the flash drum number 2  
passed through a booster 39 heat exchanger 37 and 35 and back to the  
superheater 41. It is repressurized reheated and superheated before  
10 recycled to the supercritical water heater 41.

While specific embodiments of the present invention have been  
shown and generally described above, many variations are possible.

For example, the separation of the volatile liquid organics  
formed during the reactions with water at the critical density can be  
15 carried out under varying conditions. For example, steam stripping  
at atmospheric pressure can be used to remove the volatile organic  
liquids from the water in the reaction vessel after the reaction  
or in a subsequent vessel in processing. Distillation in a distilla-  
tion tower can be carried out at pressures ranging from atmospheric  
20 to on the order of a 150 atmospheres to separate the liquid organic  
products from the water. The volatile organics can be collected  
in the vapor phase along with water to leave volatile organic residuals  
in the liquid phase after the reaction as for example at temperatures  
of from 250 to 350°C at 30 to 150 atmospheres. This can be followed  
25 by a distillation step in a distillation tower to separate the volatile  
organic liquids from the water. Flashing can be used at temperatures  
in the range of 300 to 350°C to take off gaseous products. Mem-  
brane separation such as reverse osmosis can be used to separate  
volatile organic liquids. The volatile organic liquids being highly  
30 hydrophilic, require the separation step and are produced in sufficient





- 1 quantity to make separation feasible. Preferably, the volatile organic liquids are produced in quantities at least as high as 25% but more preferably at least as high as 50% of the original organic feed.



## CLAIMS

- 1        1. A process for treating an organic material by reacting said  
organic material in water to restructure said organic material,  
said process comprising admixing feed organic material with water  
to form a reaction mixture and reacting said organic material for a  
5        time period while maintaining said water in the region of its critical  
density to form resulting organic material which resulting organic  
material is a useful volatile organic liquid.
- 1        2. A process in accordance with the process of claim 1 wherein  
said organic material in the reaction mixture is present in an amount  
of no more than 25 weight percent.
- 1        3. A process in accordance with the process of claim 1 wherein  
said process is carried out without significant char formation by  
assuring that said reaction mixture is brought to reacting temperatures  
rapidly.



1        4. A process in accordance with the process of claim 1 and further comprising,

separating resulting organic liquid from said water to recover at least 25 weight percent of the feed organic material.

1        5. A process in accordance with the process of claim 4 wherein  
said resulting organic material is a useful volatile organic liquid  
and said separating step is carried out by use of a separation technique  
selected from the group consisting of, distillation, flashing, decanting  
5 and membrane separation.

1        6. A method in accordance with the method of claim 5 wherein  
said reaction mixture is brought to reacting temperature of at least  
about 374°C rapidly and formation of char is minimized.

1        7. A process in accordance with the process of claim 6 wherein  
said reaction mixture is maintained at said reaction temperature for  
a period of time less than 15 minutes.

1        8 . A process in accordance with the process of claim 7 wherein  
said density is in the range of from .2 to .7.

1        9 . A process in accordance with the process of claim 8 wherein  
the concentration of said feed organic material in said reaction  
mixture is no higher than 25 weight percent and said reaction is  
carried out continuously in a flow through reactor.



- 1           10. A process in accordance with the process of claim 1 where-  
in the concentration of said feed organic material in said reaction  
mixture is no higher than 25 weight percent and said reaction is car-  
ried out continuously in a flow through reactor.
  
- 1           11. A process in accordance with the process of claim 6 where-  
in the concentration of said feed organic material in said reaction mix-  
ture is no higher than 25 weight percent and said reaction is carried  
out continuously in a flow through reactor.
  
- 1           12. A process in accordance with the process of claim 5 where-  
in said process is carried out in a continuous flow through reactor,  
with a feed organic material no higher than 25 weight percent of said  
water and said reaction mixture is brought to reaction temperature  
5   in a time period of less than 2 minutes.
  
- 1           13. A process in accordance with the process of claim 1 wherein  
said organic feed material is mixed with said water by heating said  
water to a temperature in the range of from 600 to 900°C and  
adding said feed organic material thereto by direct mixing in a con-  
5   tinuous flow system to substantially instantaneously raise said feed  
to a temperature of at least 374°C whereby the formation of char  
during said reacting is minimized.



1        14. In a process of forming a reaction mixture from an organic  
feed and water at a density in the critical region of water, the  
improvement comprising,  
         heating water to a temperature in the range of from 600°C  
5       to 900°C and intermixing said water with said organic feed at a concen-  
tration of said organic feed of no more than about 25 weight percent  
to form a reaction mixture at a lower temperature in the near critical  
region of water and then permitting said mixture to react to form  
reaction products.

1       15. The improvement of claim 14 wherein said organic feed is  
reacted at said last-mentioned temperature for a period of time no  
greater than fifteen minutes to obtain a volatile organic liquid reac-  
tion product in an amount of at least 25% of said organic feed.

1       16. The improvement of claim 15 wherein said water is heated  
to a temperature in the range of from 600 to 900°C by oxidizing  
a portion of reaction products obtained from said reaction mixture  
to furnish heat energy for said heating.

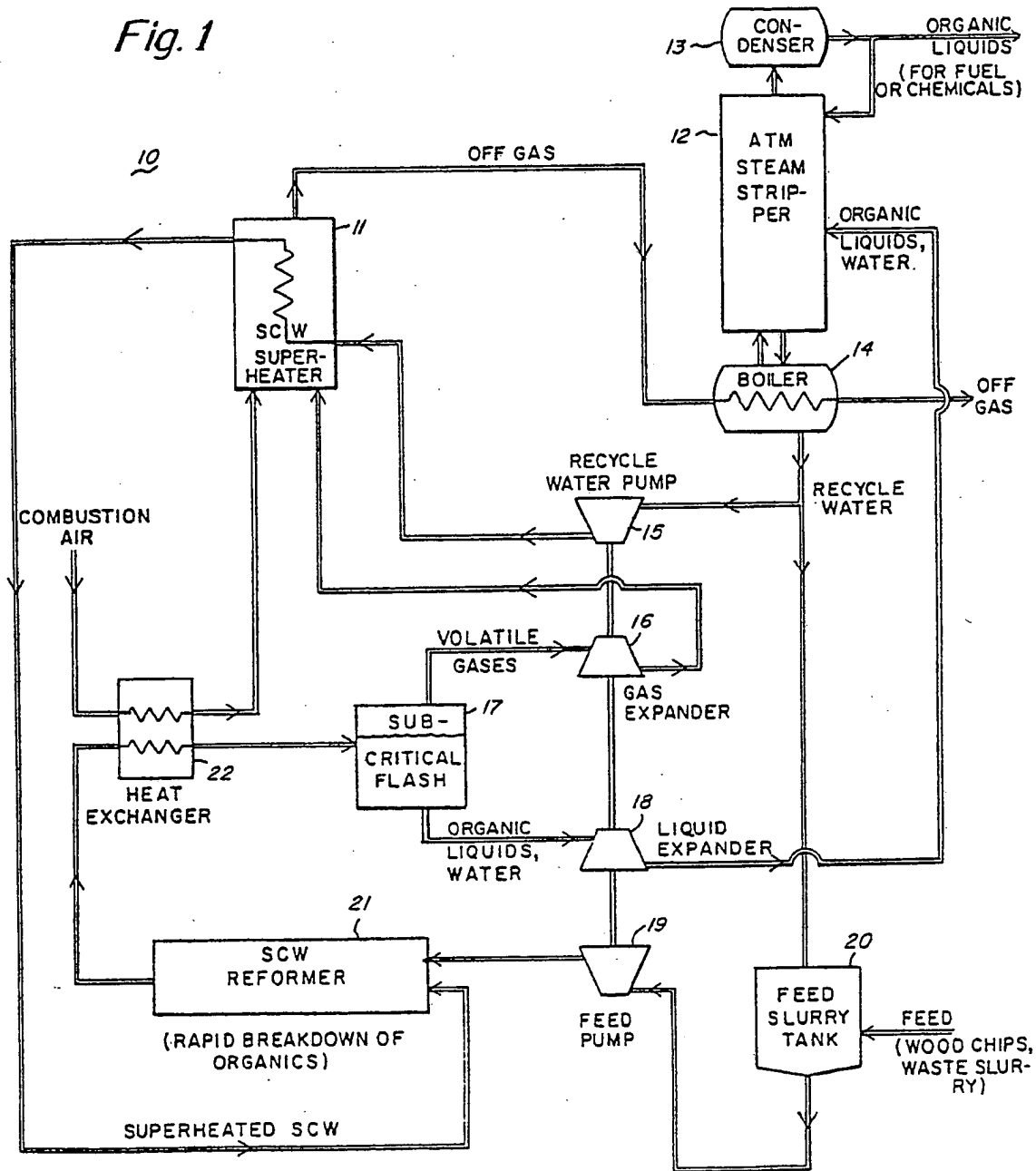
1       17. A process of treating a mixture of organic and inorganic  
materials wherein a feed of organic and inorganic materials are ad-  
mixed with water to form an aqueous reaction mixture, and a reaction  
carried out in the region of the critical density of water,  
5       the steps comprising bringing the reaction mixture to conditions  
below the critical region of water after said reaction,  
         and separating gaseous products and volatile liquids from an  
aqueous mixture of inorganic materials.



- 1        18. The process of claim 17 wherein said first-mentioned mixture is black liquor from pulping.
- 1        19. A process in accordance with the process of claim 17 wherein said process is carried out without significant char formation by assuring that said reaction mixture is brought to reacting temperatures rapidly.
- 1        20. A process in accordance with the process of claim 17 and further comprising,  
         separating resulting organic liquid from said water to recover at least 25 weight percent of the feed organic material.
- 1        21. A process in accordance with the process of claim 1 wherein said water is heated to a temperature in the range of from 600 to 900°C by oxidizing a portion of reaction products obtained from said reaction mixture to furnish heat energy for said heating.

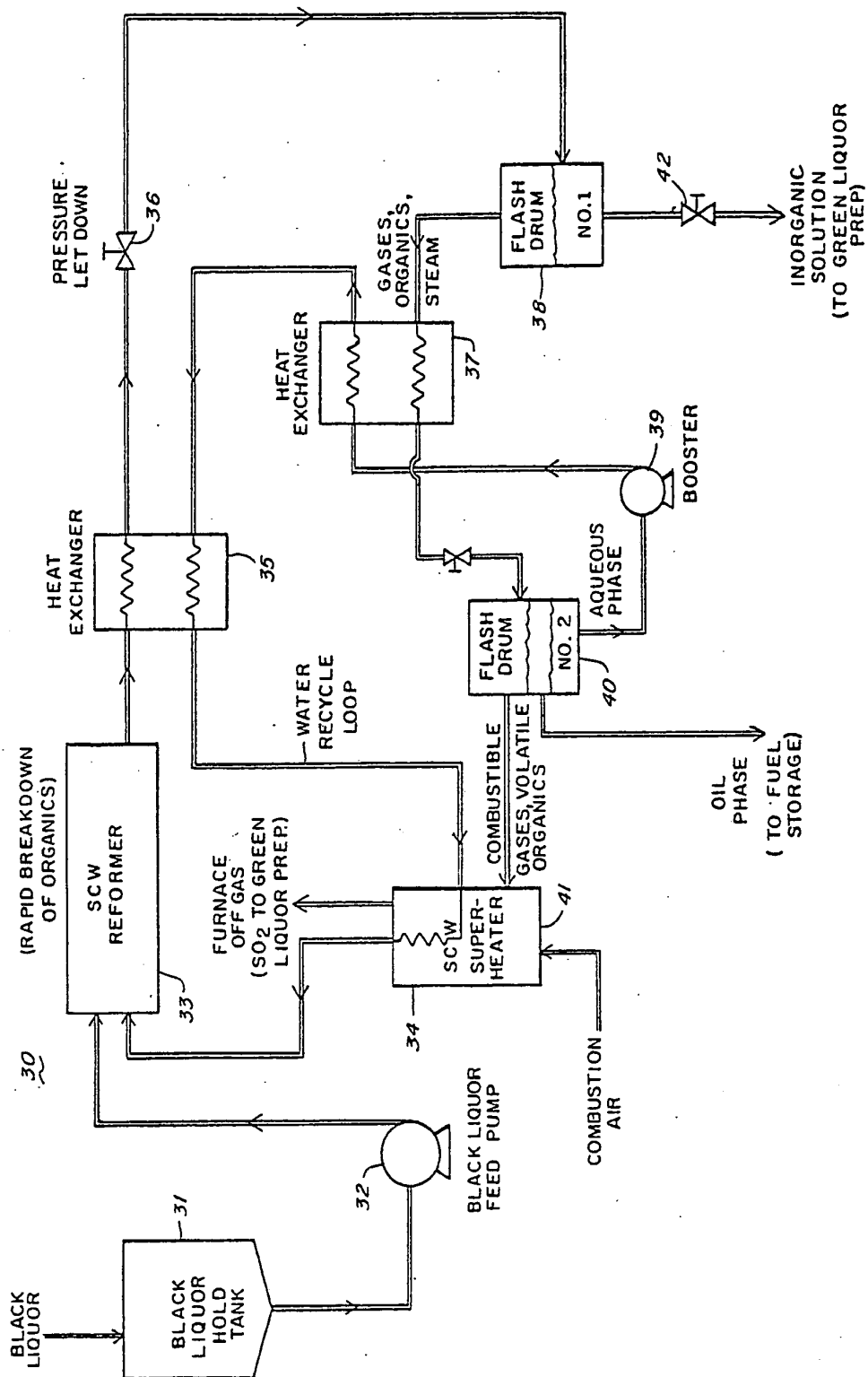


Fig. 1



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Fig. 2





# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 80/01215

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>1</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. C10L 1/00		
US. CL. 44/50		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
US	44/50	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>6</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
X	US, A, 4,113,446, Published, 12 September 1978, Modell et al	1-5
A	US, A, 4,145,188, Published, 20 March 1979, Espenscheid et al	1-5
A	US, A, 3,148,227, Published, 08 September 1964, Hearon et al	1-5
A	US, A, 3,715,195, Published, 06 February 1973, Tassoney et al	1-5
A	US, A, 3,890,113, Published, 17 June 1975, Child et al	1-5
A	US, A, 3,929,431, Published, 30 December 1975, Koh et al	1-5
A	US, A, 3,926,583, Published, 16 December Rostrup-Nielse	1-5
A	US, A, 3,919,113, Published, 11 November 1975, Reynolds	1-5
<p><sup>6</sup> Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>	Date of Mailing of this International Search Report <sup>3</sup>	
22 JANUARY 1981	19 FEB 1981	
International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>10</sup>	
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